

THE USE OF SINGLE PHOTON COUNTING METHODS  
IN SOLVING BASIC PROBLEMS  
IN CHEMILUMINESCENT REACTIONS

by

John A. Emerson

A Thesis Submitted to the Faculty  
of the Department of Chemistry  
in Partial Fulfillment of the  
Requirements for the Degree of  
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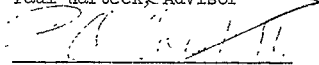
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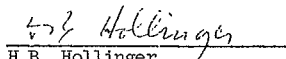
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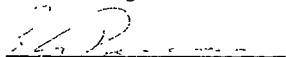
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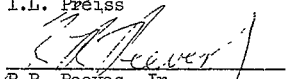
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## FOREWARD

This work started when I asked Dr. Reeves a question on a paper by Dalgarno (see Ref. 21). The paper discusses simultaneous two-photon emission in  $\text{Li}^{+2}$  and at that time I did not understand what was meant by two-photon emission. After some discussion it became apparent that we could now look for a two photon emission process on a readily available liquid scintillation counter. Shortly, thereafter, we were running samples of various gasses in quartz vials excited by a Telsa coil using the liquid scintillation spectrometer in coincident and non-coincident mode. Therefore, we could get the singles rates as well as the coincidence rate. One particular sample, solid sulfur and oxygen, when excited with a Telsa coil for 15 seconds gave such a high emission intensity for the first hour, that the electronics were effectively flooded and we could not register a single count on the system counters. This was not all expected because the same sample had been measured earlier with a low-noise level photomultiplier with a continuous output, but the signal had decreased to the noise level of the instrumentation within 3-4 minutes. We knew this was not only a simple readily available arrangement but also a very sensitive one for measurement of low-light levels.

In the course of these luminescent studies, we have presented two papers on low-level emissions in chemiluminescence reactions which to our knowledge represents the only work done with a single-photon apparatus studying this type of reaction. Dr. Reeves suggested that I should make an attempt to look for the dual emission in the  $\text{SO}_2$  afterglow. Since our earlier work with the liquid scintillation system did not reveal the dual emission, only by optimizing the reaction flow pattern, geometry, and the electronics was a dual emission observed.

Apparently, the idea that a type of two photon emission could help explain the disagreement of various workers on the kinetics of the air afterglow had been discussed by Harteck and Reeves several years earlier. We hope that the concept of dual emission will clarify the interpretation of earlier works and be extended into other areas of chemical kinetics.

## ABSTRACT

A combination of single photon counting and a fast coincidence system found in nuclear physics experiments permit the observation of a dual emission process in a two body luminescent reaction. The lifetime of the excited  $\text{SO}_2$  species produced in the  $\text{SO} + \text{O}$  reaction has been measured. The process involves the emission of a primary photon from a collisional complex of relatively short lifetime ( $< 10^{-12}$  sec.) This leaves an excited state which then may emit another photon. The  $\text{SO}_2$  molecule so produced may not be in the ground vibrational state but in a state which is in the order of 0.1 eV to 0.2 eV above the ground state. By analogy, it is concluded that similar reactions may follow the mechanism proposed.

The first experiments conducted consisted of a coincidence analyzer with a flow system. The results were satisfactory, but the lifetime of the excited species was difficult to obtain. More precise results were obtained with further refinements in the electronics including use of a delay coincidence system and multichannel analyzer, and also with modifications of the reaction flow system itself.

The dual emission was therefore observed in several different experimental arrangements. From a practical standpoint - enough data could be taken in the later arrangement in a few minutes to equal a full day of data taken by the previous system. The primary region of the spectrum where the dual photons are emitted appears to be about 4000 $\overset{\circ}{\text{A}}$ -4500 $\overset{\circ}{\text{A}}$ . The average lifetime of the excited species is now estimated as approximately 10 nanoseconds.

## PART I

## INTRODUCTION

Several recombination reactions of atoms with diatomic molecules are known to yield electronically excited products; for example  $\text{SO} + \text{O}$ ,  $\text{CO} + \text{O}$ , and  $\text{NO} + \text{O}$ . These reactions are characterized by emission spectra which appear continuous both at low and high dispersion.<sup>1</sup> It has been shown that most of these reactions at low pressures proceed by a radiative two-body recombinations.<sup>2-13</sup> However, a controversy exists as to whether these chemiluminescent reactions are a two- or three-body process at pressures below 1 Torr.<sup>14</sup> The present work gives support to the hypothesis that the two-body process is correct by presenting evidence that a dual emission process is a principle part in the mechanisms of the reactions mentioned above. Although an earlier attempt to find dual emission by using a static system had failed,<sup>15</sup> it was felt that an increase in the sensitivity of the electronics and the addition of a flow system might increase the possibility of observing the dual emission process. Knowing that newer equipment for the observation would still be at the threshold for sensitivity, another attempt was made by looking at the most promising  $\text{SO} + \text{O}$  atom reaction afterglow. The criteria considered reasonable for the dual emission process were: (a) intensity versus wavelength curve should be shaped like a beta curve and the spectrum should show little structure but be continuous; (b) the energy of the reaction should equal the lower wavelength break of the chemiluminescence curve; (c) complement-photon emission is observed in atoms; and (d) the kinetics by various investigators had shown that reactions were a two-body collisional process.<sup>2-13</sup>

### A. Complement-Photon Emission in Atoms

The continuum resulting from  $2S \rightarrow 1S$  transition in the atomic hydrogen complement-photon (simultaneous two-photon) emission is considered to be one of the important processes in the hydrogen atom recombination continuum observed in planetary nebulae.<sup>16</sup>

Breit and Teller<sup>17</sup> consider the mean life of the  $2S$  state of hydrogen in the absence of collisions, as primarily due to simultaneous emission of two photons. Lipeles, Novick and Tolk<sup>18</sup> have used coincidence counting techniques to detect the complement photon decay of the metastable  $2^2S_{1/2}$  state of singly ionized helium. Further work<sup>19</sup> in studying the emission from the metastable  $2^2S_{1/2}$  by means of a broad-band spectroscopic coincidence counting technique have shown that the spectrum is continuous and that spectral distribution is symmetric for the complement-photon process. Artura et al suggest that complement-photon emission from the metastable  $2^2S_{1/2}$  state of  $He^+$  must be considered significant for the continuous-emission spectra of planetary nebulae and related astrophysical phenomena.<sup>19</sup>

Griem and co-workers<sup>20</sup> observed in the soft x-ray region a (a) continuum emission associated with radiation from the complement-photon decay of the  $2^1S$  metastable state of helium like Ne IX. Victor and Dalgarno<sup>21</sup> have shown by calculation that complement-photon emission from the  $2^1S$  metastable state of singly ionized lithium would have a continuous distribution broadly peaked at 30 eV.

In addition, the time correlation between cascading emitted photons in the mercury atom has been measured.<sup>22,23</sup> The direct measurement of the lifetime of the  $6^3P_1$  state of mercury was achieved by examining the successively emitted photons in the  $7^3S-6^3P_1-6^1S_0$  cascade of atomic mercury with a delayed coincidence counting system.

## B. Recombination Reactions

Most studies of the chemiluminescent recombination reactions have involved ground state atoms reacting with the ground state molecule.

For the purpose of this work only three of these reactions



will be considered for discussion and only reactions 1 and 2 were studied.

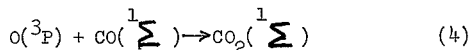
### 1. NO + O Reaction

The release of nitric oxide in the upper atmosphere was used to measure the relatively high concentration of oxygen atoms in the chemosphere.<sup>24,25</sup> Due to the low pressure in the region two-body reactions would be dominant over the three-body. Also the NO + O reaction can be used as a standard from which absolute rate constants for other chemiluminescent reactions can be determined.<sup>26</sup> Of the three reactions discussed in this work, the NO - O afterglow has received the greatest attention and is also the most controversial. Three independent laboratories have measured the rate constant for reaction (3) at low pressure using the stirred flow reactor technique.<sup>6,8,27</sup> Several other researchers have found conflicting results; e.g. some <sup>\*The results given in a paper by Becker<sup>27</sup> et al show the NO<sub>2</sub> emission</sup> to be dependent upon total pressure in the region of 2-25 mTorr. This was in a relatively small vessel where possibly back diffusion was not negligible. However, in a later publication<sup>9,10</sup> their findings show using the immense 2.5 x 10<sup>5</sup> liter vessel now in operation the NO<sub>2</sub> emission to be pressure independent in the mTorr region.

data indicates that the intensity of NO and O is dependent on pressure in the low pressure region. The erroneous results may be attributed to improper experimental conditions such as "over-titration" or (neglect of) back diffusion. One assumption that three groups base their results on is that the radiative lifetime of NO<sub>2</sub> fluorescence is 44 microseconds, as indicated by published data. The results are obtained by assuming a Stern-Volmer mechanism; however recent results show that the slope is not constant at low pressures as it is at high pressures.<sup>32</sup>

## 2. CO + O Reaction

The reaction of carbon monoxide and oxygen is of special significance in the understanding of carbon monoxide flames and explosions and of the photodissociation of carbon dioxide in the Venus atmosphere. Two reactions can occur: one produces ground state CO<sub>2</sub> the other produces electronically excited CO<sub>2</sub> which is responsible for the chemiluminescent radiation. The mechanism of radiative oxidation has been the subject of much disagreement, which has centered around the question of whether the reaction is bi-<sup>3,4,11,12</sup> or termolecular.<sup>33</sup> This question apparently arises over the spin-forbidden nature of the overall reaction

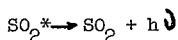
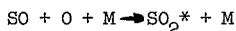


which, unlike other chemiluminescent reactions, has a positive activation energy of about 3 Kcal/mole (0.13 eV).<sup>33,34</sup>

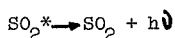
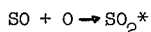
## 3. SO + O Reaction

The deep blue emission of the sulfur dioxide afterglow was observed in 1931 in the reaction of oxygen atoms with hydrogen sulfide.<sup>35</sup> In 1934 Gaydon<sup>36</sup> studied the afterglow by passing a low-frequency discharge

through flowing  $\text{SO}_2$  at 0.1-5 Torr. He found that the emission was a continuum and could be attributed to electronically excited  $\text{SO}_2$  resulting from combination of  $\text{SO}$  and oxygen atoms. The kinetics of the reaction of oxygen with  $\text{H}_2\text{S}$ ,<sup>38,40</sup>  $\text{COS}$ ,<sup>5,37,38,41</sup> and  $\text{CS}_2$ <sup>37,38,39</sup> have been studied only recently. In all cases, the deep blue emission that takes place can be explained by the formation of  $\text{SO}$  radicals which then react with excess  $\text{O}$  atoms. The chemiluminescent reaction of  $\text{SO}$  and  $\text{O}$  at pressures below the 1 Torr range have been studied. From limited results which are difficult to reproduce this reaction is third order at pressures below one Torr and occurs by the following mechanism,<sup>42</sup>



while others consider it to be second order:<sup>5,43,44</sup>



### C. Emission and Energy

The intensity versus wavelength curve for the afterglows of  $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{NO}_2$ <sup>26</sup> are shown in Figure 1. All three curves have been normalized, i.e., the relative intensity axis has arbitrary units. The shape of these curves very closely resembles the shape of the energy-versus-intensity curve observed when an antineutrino and a beta particle are emitted from a nucleus. A continuum which goes through a maximum is characteristic for both types of curves. Also the chemiluminescence for each afterglow breaks off at the energy required for formulation of the triatomic molecule from the diatomic molecule plus an atom. The

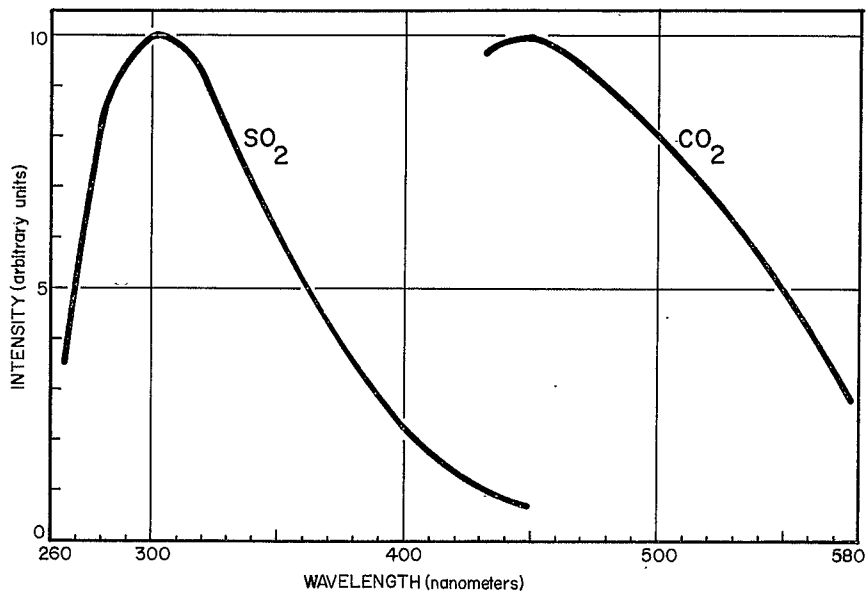


FIGURE 1A SPECTRAL DISTRIBUTION OF SO<sub>2</sub> AND CO<sub>2</sub> AFTERGLOWS

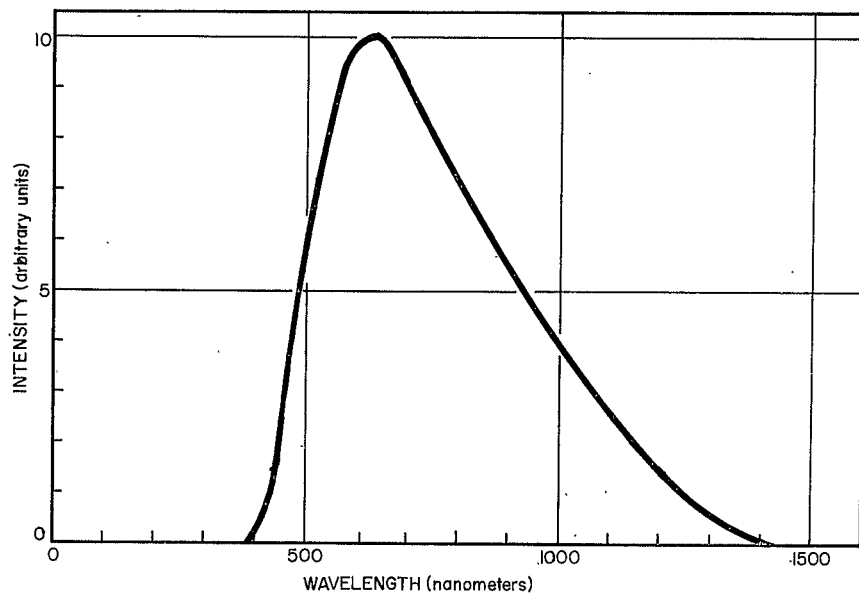
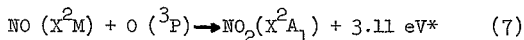
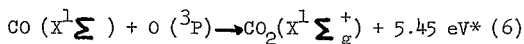
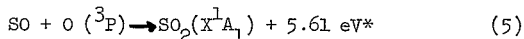


FIGURE 1B SPECTRAL DISTRIBUTION OF THE NO<sub>2</sub> AFTERGLOW

energy of each reaction and its corresponding wavelength is given.<sup>48</sup>



#### D. Purpose of the Investigation

Many problems may still exist in fully understanding the kinetics of reactions 1-3. The above discussion is included only to give this thesis some flavor of the disagreements that exist. Basically, several researchers' results may be erroneous because of poor experimental practices. However, it is not the intent of this work to repeat previous work for further refinements, but to introduce a new parameter that is necessary to interpret the kinetics properly. Ergo, the purpose of this research is:

1. To employ single photon counting techniques with different methods of measuring the short time interval between photons emitted from excited molecules formed in a two-body reaction.
2. To investigate how certain chemiluminescent reactions take place.
3. To evaluate further the claim that reactions 1-3 are second order below 1 Torr, in light of the experimental work reported herein.

\*Energies converted to wavelength are listed in Table I.

TABLE I

Conversion of electronic volts to wavelength reaction

<u>Equation No.</u>	<u>Dissociation Energy</u>	<u>Wavelength Limit</u>
5	5.61 eV	<sup>o</sup> 2210A
6	5.45 eV	<sup>o</sup> 2280A
7	3.11 eV	<sup>o</sup> 3990A

## PART II

## EXPERIMENTAL

A. Preparation of Materials

Various gases including ultra high purity oxygen ( $O_2$ ), carbonyl sulfide ( $COS$ ), nitric oxide ( $NO$ ), carbon monoxide ( $CO$ ), 10%  $O_2$  - 90% argon ( $Ar$ ) mixture, and 10% nitrogen ( $N_2$ ) - 90% oxygen ( $O_2$ ) mixture were obtained from the Matheson Company, East Rutherford, New Jersey.

$CO$  was purified by passing it through a saturated solution of sodium hydroxide to remove the iron carbonyl and then through a series of liquid oxygen traps to remove condensibles and the purified gas was transferred into a glass storage bulb.

Carbon disulfide ( $CS_2$ ) was obtained from the B and A Company, a division of Allied Chemical, and used without further purification. The introduction of  $CS_2$  into a storage vessel as a gas was done by evaporating the liquid  $CS_2$ , and passing the vapor through a leak into a glass storage blub. To remove any air which may have contaminated the  $CS_2$  in the transferal from the storage bottle to the vacuum system, the  $CS_2$  was frozen solid at Dry Ice temperature and pumped on for 30 minutes.

The purity of  $O_2$  was better than 99.85% with trace amounts of  $N_2$  (4.8ppm), water ( $< 2$ ppm), xenon (0.6ppm) and krypton (13ppm).

The 10%  $O_2$  - 90%  $Ar$  and 10%  $N_2$  - 90%  $O_2$  - mixtures and the  $COS$  were used without further purification. The  $NO$  was purified by bulb-to-bulb distillation until a white solid was obtained at liquid nitrogen temperature.

## B. Apparatus

### 1. Vacuum System

The chemiluminescent reactions were carried out in the experimental arrangement shown in Figure 2. About 5% O-atoms were produced in a Wood-Bonhoeffer glow discharge tube; the gas stream was then pumped through the reaction tube into a 22-liter Pyrex sphere which acted as a stirred flow reactor. Part of the flow leaving the sphere was by-passed through a smaller tubing as shown in Figure 2. An additional by-pass in this section included a 4mm ID Pyrex tube, a section of which had two photomultipliers mounted on either side. A small segment of the 4mm tubing was used as the specific reaction volume under study.

The pumping system consisted of a 4-inch glass cold trap cooled by liquid oxygen, followed by a CVC model MHG 50, mercury diffusion pump backed with a Welch Model 1397 pump. A similar arrangement, but without the 22-liter sphere, is shown in Figure 3. A side arm was attached where the radicals and atoms could diffuse into the region of observation. This region was a dead end 2mm ID Pyrex tube, and the two photomultipliers were mounted, one on either side.

### 2. Mass Spectrometer

A CEC 21-130 mass spectrometer was used for gas analysis.

### 3. Pressure Measurement

An alphanatron model 530 vacuum gauge made by Norton Vacuum Equipment Newton, Massachusetts, was used for pressure measurements. All readings from the instrument were multiplied by a correction factor of 0.855.

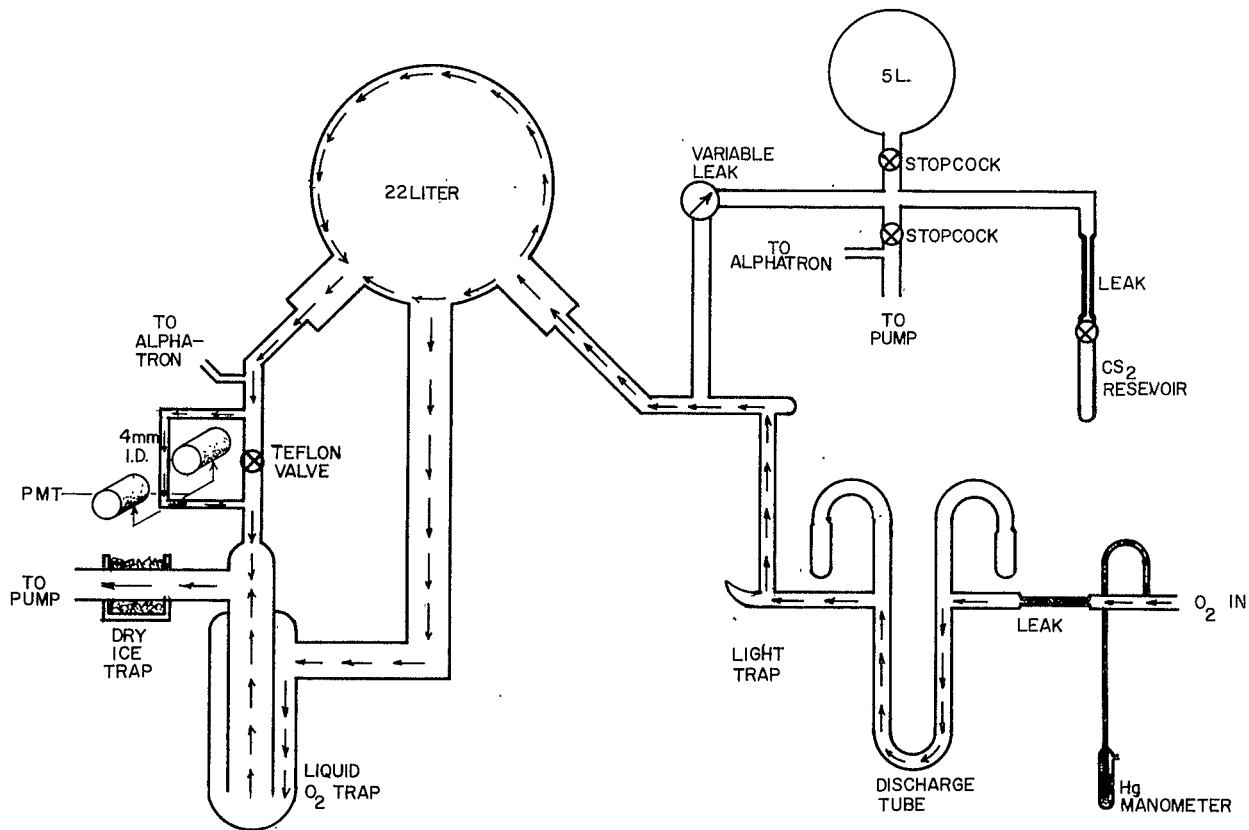


FIGURE 2 VACUUM ARRANGEMENT FOR SYSTEM ONE

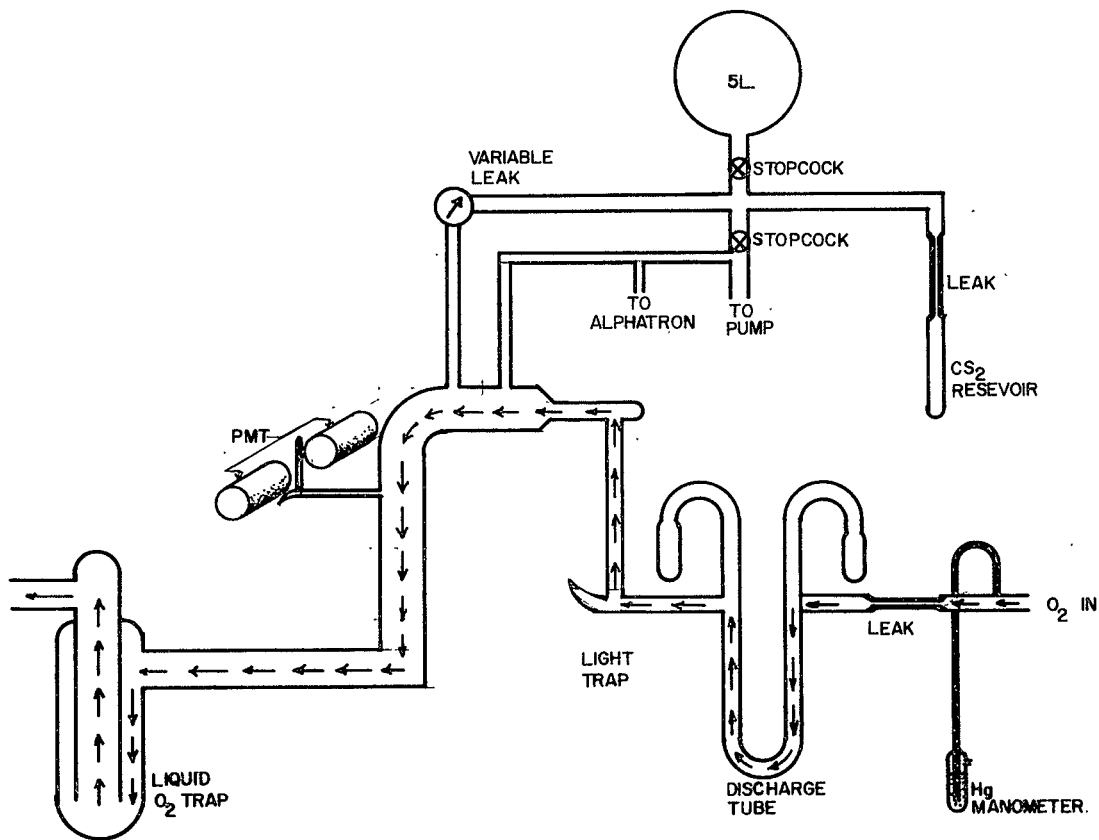


FIGURE 3 VACUUM ARRANGEMENT FOR SYSTEM TWO

#### 4. Glow Discharge

A Wood-Bonhoeffer discharge tube<sup>49,50</sup> with aluminum electrodes was used to dissociate some of the molecular oxygen into atomic oxygen. No material was added to poison the walls of the discharge tube. The power supply for the AC discharge consisted of a high-voltage transformer, the primary circuit in series with a Variac for controlling power input, and a limiting resistor. A watt meter was used for measuring the power input. The secondary winding was connected to the electrodes of the discharge tube. Power input for all experiments was between 400-900 watts.

#### 5. Photomultiplier Assembly

The detector for the light emission was a RCA-8575 12-stage, 2-inch head-on-type of photomultiplier tube. The spectral response for the tube is given in Figure 4.<sup>51</sup> The 8575 was selected for fast coincidence counting because of the fast response, high current gain, relative freedom from after-pulse and the small spread in electric transit time. With a supply voltage of 2400 VDC, the following characteristics<sup>51</sup> of the 8575 are: anode-pulse rise time - 2.4 nanoseconds (nsec.), current amplification -  $10^7$  and electron transit time - 34 nsec. The socket end of the tube is made light-tight with a boot furnished by RCA. The photomultiplier base assembly is illustrated in Figure 5 and includes: a mechanical base, a resistor voltage-divider network, a mu metal magnetic shield, a filter holder and shutter. Two types of resistor networks were used. The first was the type supplied commercially by Ortec of Oak Ridge, Tennessee, a Model 265 photomultiplier base which gave a dc-coupled, back terminated, negative 50 ohm timing signal. Internal trimmer controls permitted optimum adjustment of the voltage

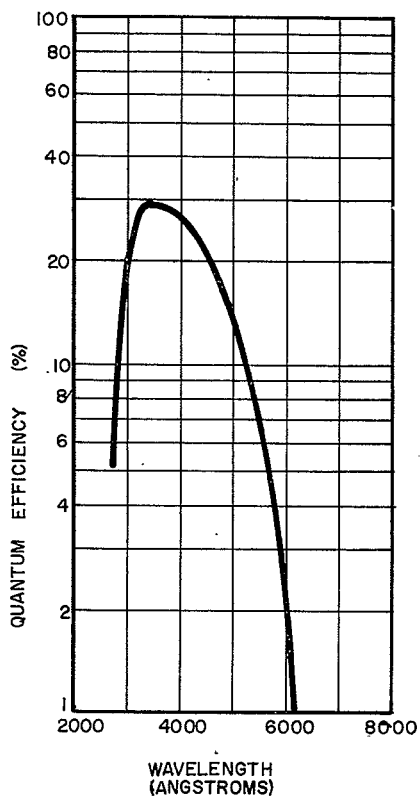


FIGURE 4 SPECTRAL RESPONSE OF THE 8575  
PHOTOMULTIPLIER TUBE

distributed to the focusing electrode, and the second and twelfth dynodes. The other resistor network was constructed from the schematic furnished by RCA,<sup>51</sup> where only a focusing control was available. The rise-time of the dc-coupled anode pulse was matched to that obtained from the Ortec base by use of capacitors across the dynode stages of the tube. For convenience generally the Ortec circuit was used for one tube while RCA network was used for the other.

#### 6. Fast Coincidence Timing System

Some of the problems using the instrumentation in observing the dual emission process might not be familiar to the average researcher, thus a description of the standard equipment used is given below. The designing and manufacturing of this type of nuclear equipment by various companies is subject to the NIM standard\*. Although this standard does exist, interfacing equipment of various manufacturers does warrant caution.

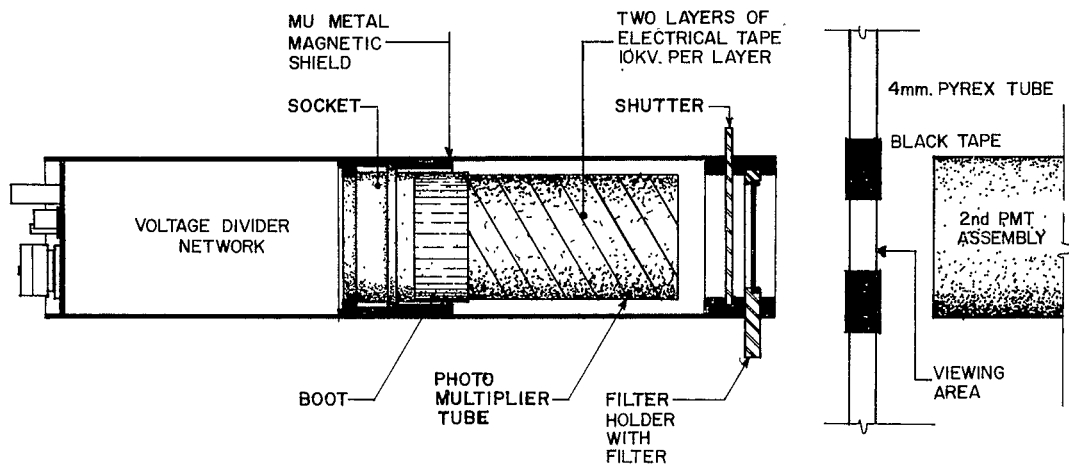
A block diagram of the fast coincidence system used is shown in Figure 6. All of the NIM equipment used required a power supply and a bin for plugging operations in the modules. Bin Model 1400 of Canberra, Meriden, Connecticut, and Hewlett Packard Model 5580B served this purpose.

#### Amplifier

A Linear Amplifier Model 133 from LeCroy System, West Nyack, New York, consisted of two high-speed direct-coupled pulse amplifiers. Each of the 133's channels are independent consisting of a 10-step

\*NIM(Standard) is a short notation for Nuclear Instrument Module

Standard where the standards for compatibility between instrument makers are published in USAEC Report TID-20893 (Rev.).



NOTE: NOT TO SCALE

FIGURE 5 PHOTOMULTIPLIER BASE ASSEMBLY

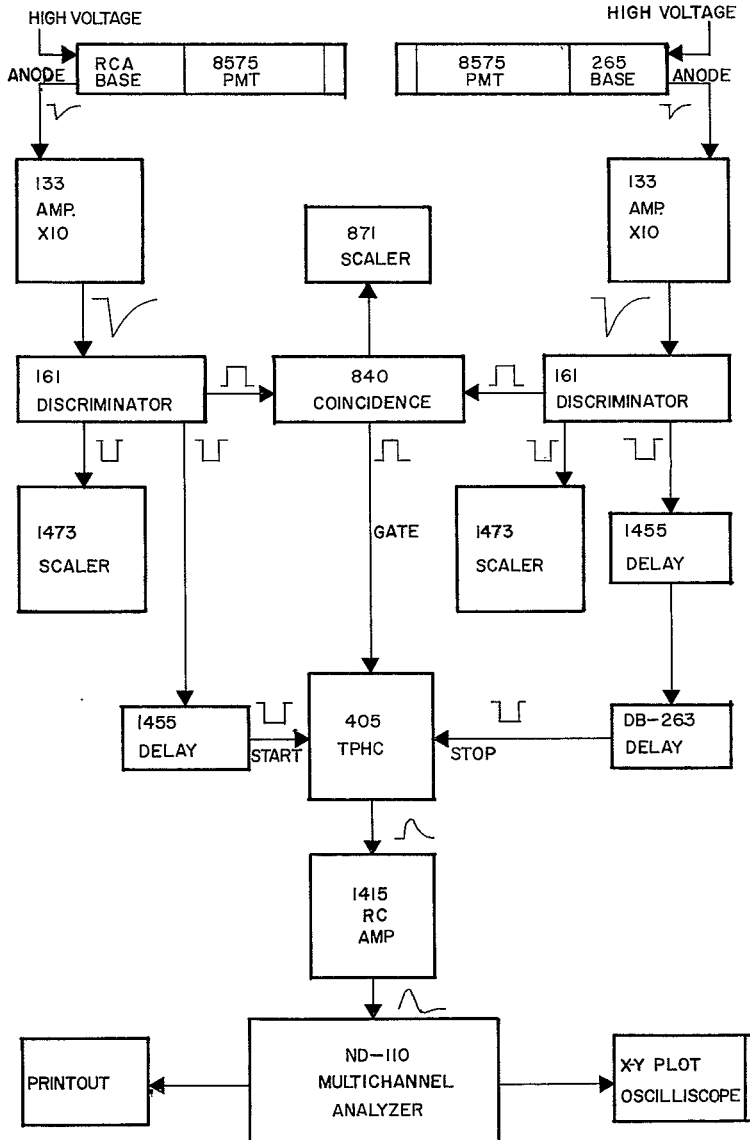


FIGURE 6 FAST COINCIDENCE SYSTEM

50 ohm attenuator and a basic direct-coupled solid-state amplifier. Both input and output DC levels are at ground potential. Separate capacitively coupled AC inputs can be used for DC blocking. The unit has a gain bandwidth product of 2000 MHz (Megahertz) and features: rapid overload recovery, stable baseline, and general freedom from spurious effects.

#### Discriminator

LeCroy System Model 161 Discriminator is a dual, fixed threshold, leading edge, pulse amplitude discriminator with a bandwidth of 150 MHz. The minimum double-pulse resolution is 6 nsec thus giving the capability of no multiple pulsing. An output occurs whenever an input pulse exceeds the input threshold of 100 millivolts (mV). The duration of logic output can be set continuously from 3 to 150 nsec, and is independent of input pulse duration, amplitude, and rate. One complement and two negative outputs of 750 mV are delivered simultaneously in parallel, each of which may be fanned out, terminated, or clipped.

#### Scaler and Timers

Canberra Model 1473 Scaler and Model 1492A Timer/Scaler were used for measuring the singles rates of each channel. The 50 ohm negative input had an adjustable discriminator that can be set to handle various pulse height from -200 mV to -2 volt for the input. The DC Coupled input had a 5 nsec minimum pulse width thus allowing scaling spreads of over 20 MHz. An overflow 5 volt pulse was available as an output at reset of sixth decade. The capacity of the display was six decades, allowing a maximum count of  $10^6 - 1$ . Electronic gating capability could be used with an input of 3 to 10 volts DC which enabled accumulation. Other controls available for operation were start, stop and reset.

Canberra 800 series scalers were designed for elementary counting systems. The input required was 1.5 to 10 volt,  $\geq 50$  nsec pulse width with repetition rate of less than 30 KHz. The capacity of display was three electronic decades and six mechanical decades allowing a count of  $10^9-1$ . Electronic gating capability was the same as for the 1400 series scaler described above. The manual operations included start, stop and reset.

Canberra Model 891 Electromechanical Timer was used to control the present time of the scaler with a gating pulse. The ability of setting the timer repeatably was 0.01 minutes. The gate output was an open circuit when running and short circuit when stopped. This timer is a Geibel-Flarschein type employing a synchronous motor controlled by line frequency. Also a Canberra Model 890 Scaler/Timer was used occasionally for controlling duration of counting.

#### Coincidence Analyzer

A Canberra Model 840 Coincidence Analyzer accepted up to four positive pulse inputs. In turn, it produced a positive logic pulse output of duration of 1  $\mu$ sec when the inputs occur within the resolving time set by controls, i.e., when the leading edges of all selected input logic pulses occurred within a time period called the resolving time. Two resolving time ranges are provided: 10-100 nsec and 0.1-1.0  $\mu$ sec.

#### Delays

Canberra Model 1455 Logic Shaper and Delay accepts any positive or negative 0.7 to 12 volt input signal and, in turn generates six simultaneous 0.1 to 11  $\mu$ sec delayed outputs. The nonlinearity of the adjustable delay was less than  $\pm 0.5\%$ . The fast output produces a

600 mV pulse with a risetime less than 5 nsec, a width of less than 20 nsec; output impedance of 50 ohms.

E.G.G., Salem, Massachusetts, Model DB-263 Delay Box was a 50 ohm calibrated cable delay which provided relative delays of 0 to 31.5 nsec in 0.5 nsec increments with a 50 ohm termination. The adjustable delay accuracy of each switch calibration was better than  $\pm 0.1$  nsec. Reflections at any delay setting were less than 3% for risetime step of 1 nsec.

#### Time to Pulse Height Converter

An Ortec Model 405 Time to Pulse Height Converter (TPHC) accepts 0.5 volt negative signals at its start and stop inputs. A TPHC is in reality a differential coincidence unit where the time scale is converted to a pulse height scale, thereby allowing time analysis by means of slower linear circuitry. The operation of this Model 405 TPHC is as follows.<sup>52</sup> The start pulse is amplified and inverted, and sets a tunnel diode memory to the "one" state. The stop pulse is amplified, and resets the tunnel diode memory back to the "zero" state. While the tunnel diode memory is in the "one" state, a constant current flows to charge a fixed capacitor. The voltage on this fixed capacitor is directly proportional to the time between the start and stop pulse and is presented as an output. Five ranges of measurement are possible: 0.125, 0.25, 0.5, 1.0, and 2.0  $\mu$ sec full scale. A positive gate input pulse of 2-10 volts 1  $\mu$ sec wide enables the start input when TPHC is in a gated mode.

#### RC Amplifier

Canberra Model 1415 RC Amplifier was a low noise level, double delay line, clipping, linear amplifier with pole zero cancellation. A gain of 2.4 to 1000 was possible with integral nonlinearity of less than 0.1%.

### Multichannel Analyzer

A Nuclear Data, Palatine, Illinois, Model ND-110 Channel Analyzer was a 128 channel multichannel analyzer with capability of pulse height analysis, multiscaling, and readout (graphic and numeric), being structured around an analog-to-digital converter and a special purpose digital computer. During the pulse height analysis the converter section generated a number of sequential pulses that were directly proportional to the amplitude of an analyzed input signal. The pulses were counted by a channel scaler in the computer, and the resulting number was then used to index a storage channel in the computer memory, where a count of one was added to the indexed channel. Thus, after a preset time of counting, the information could be displayed from the computer memory either in a linear or a logarithmic format as a analog plot on ancillary oscilloscope. Data also could be printed out on paper tape via a Victor Digit-Matic serial printer. The conversion time for analog to digital signal was  $2.5 \mu\text{sec}$  plus  $0.25 N \mu\text{sec}$  where  $N$  was equal to the channel number. The average storage cycle time was approximately  $25 \mu\text{sec}$  for one count to be added to channel of the memory; the maximum count capacity of each channel was  $10^5 - 1$ .

### Pulses

A LeCroy Model 1P-1 Instapulser was a battery-powered nanosecond pulse generator. The output was direct-coupled and reverse-terminated with 50 ohms, has pulse duration of 7 nsec risetime of 2 nsec and amplitude of 350 to 400 mV, and measured rep rate of 12 KHz.

### High Voltage Power Supply

A Harrison Model 6110A DC Power Supply made by Hewlett-Packard is a high-voltage, solid state supply that is exceptionally stable for

the use with photomultipliers. The DC output is adjustable from 0 to 3000 volts, with ripple and noise less than 400 microvolts RMS. The maximum current output is 6 milliamps, with a voltage stability of 0.012% per month.

### Oscilloscope

Tektronix scope models 545A, RM503 and 561 with a 3T77 sampling sweep and 3S1 sampling dual-trace plug-ins were used in this work for timing and display information. The RM503 was used as an ancillary oscilloscope for the multichannel analyzer. A permanent copy of the analog plot could be obtained by using the Polaroid camera scope attachment. The scope Model 545A with CA plug-in and Model 561 with sampling plug-ins were used for setting delays, determining shape of pulses, and checking the timing of various circuits. If the width and rise-time of signals were in the microsecond region the 545A scope was used; shorter and faster signals were monitored with the sampling instrument.

### C. Procedure

The purpose of the experiment was to perform single photon counting experiments reliably with maximum efficiency and simultaneously measure the time correlation between the photons being emitted by a complex gas phase reaction. If either efficiency of the light detection equipment or the "chemistry" of the system were not optimized, chances of seeing the dual emission were remote.

In order to ascertain that the electronic equipment would operate; two types of experiments were performed: first single photon counting via fast pulse generation; second measurements of the lifetime of the 1.332 MeV level of <sup>60</sup>Ni. The single photon counting work is described

elsewhere.<sup>15,53</sup> Briefly,<sup>28</sup> it was found that reactions could be followed where only a small fraction of the reaction resulted in chemiluminescence or where very slow chemiluminescent reactions occurred. This could include even reactions so slow that only over geological ages would they be completed. In the case of the fast gamma-gamma delayed coincidence experiment with the <sup>60</sup><sub>28</sub>Ni described in the Appendix I, experience in handling NIM equipment was gained.

### 1. The Production of the Chemiluminescence

The description of two vacuum systems is given above. In general the operation and construction of the vacuum equipment is the same as in most gas phase kinetics experiments. Great pains were taken to keep the walls of the system clean and free from sulfur products. This was done by passing 5% O-atoms at 0.5 Torr through the system for two days before running any experiments, and for at least two hours for every half hour of running time thereafter.

The production of the SO<sub>2</sub> afterglow by the reaction of O-atoms with COS or CS<sub>2</sub> is a well known process. However, it was found that an excess of O-atoms was necessary for the SO<sub>2</sub> afterglow to be formed in preference to all other possible reactions. Reactions that do occur include:





SO radicals, which are fairly stable, and solids may collect on the glass walls of the apparatus after a short period of time. Oxygen atoms can then subsequently react with the residual solid and emission is observed for long periods after the gas flow of COS or CS<sub>2</sub> is shut off. Because of the sensitivity of the light detection system, any light emission within the observation region and in the spectral range of the filter photomultipliers is counted.

The pressure of the system was adjusted by reducing or increasing the pressure on the high pressure side of the leak. A direct measure of the pressure was obtained with the Alphatron gauge. The discharge was turned on with an input power level of 500-600 watts. After the required period of O-atom cleaning, a small amount of COS or CS<sub>2</sub> was added. In the case of the apparatus shown in Figure 2, the variable leak was adjusted so that the 22-liter bulb glowed a faint blue. The Teflon valve was adjusted for the maximum single counting rate. In the other configuration as shown in Figure 3, the COS or CS<sub>2</sub> was added in minute quantities, so that the single counting rate was increased by a factor of 10-50 times over the background rate. Another method of producing the SO<sub>2</sub> afterglow in the system shown in Figure 3 was to increase by 10 times the amount COS or CS<sub>2</sub> in the

O<sub>2</sub>-Ar-O gas stream for a period of a half hour, wait up to two- or three-hours with the discharge on and then take counting data. In general this procedure gave the best results for the dual emission.

In the case of the NO<sub>2</sub> and CO<sub>2</sub> afterglows, the NO or CO was added directly to the gas stream through the variable leak and adjusted so that the counting rate was about maximized for CO<sub>2</sub> and a factor of 50 times greater than the background single rate for NO<sub>2</sub>.

## 2. Operation of Electronics

The 8575 photomultipliers were received from RCA already wrapped with two layers of electrical black tape (to prevent voltage breakdown across the glass envelope to nearby shielding and also to prevent light leakage). RCA used glass on the 8575 tube instead of a phenolic base as is frequently used on other types of photomultipliers. This thereby reduced the high voltage leakage across the connecting pins at the base. However, the base of the tube was not covered and a rubber boot furnished by RCA had to be placed over it to prevent light leakage into the tube. Care was taken not to allow fluorescent lighting to impinge upon the photocathode of the tube. The tube with boot was mounted in the socket of the base assembly. The mu metal shield was installed with felt washers between the tube and the shield. Magnetic fields are cancelled by the mu metal shield, so the photomultiplier could be moved without fear of changing performance. The filter and shutter assembly were mounted on the end of the shield. Figure 5 shows the completed assembly. The shutter was used to block any light from entering the photomultiplier, thus, once the tube was dark-adapted, reliable performance was assured.

The adjustment of the voltage divider network for optimum pulse shape of the tube was carried out before any assembly of the individual NIM modules. A six-volt light bulb with a blue filter, Corning CS 5-58, was placed into a light-tight box so that an area of only  $5 \text{ cm}^2$  of blue light was sensed by the tube.

The photomultiplier assembly was mounted next to the light source so that stray light was minimized. A DC power supply furnished a constant voltage to the light bulb. The anode output of the tube with an applied 2400 VDC was coupled by 50-ohm cable to the sampling scope. For the Ortec 265 base, adjustment of the two bleeder string controls for maximum output signal was done. This assures that the input optics are adjusted properly. The voltage on the twelfth dynode was adjusted for maximum signal output without pulse shape distortion. The adjustment of the focusing control on the RCA designed base was done in a similar manner. In this case, the output signal was maximized while minimizing the pulse distortion.

The high voltage and LeCroy Model 133 Amplifier's gain were set for maximum photon counting. Tritium counting offers a reliable way of maximizing the efficiency of the total coincidence system. To obtain the proper timing of signals, the Instapulser was connected via a tee to two 50-ohm cables coming from the photomultipliers to AC inputs of the LeCroy Model 133 Amplifier. The DC output of the 133 Amplifier was connected to the LeCroy 161 Discriminator. The complement outputs were fed to the sampling scope. By using the dual trace feature, the signals could be matched time-wise by adjusting the length of the cables. At this point the logic pulse of 161 discriminators were set to width of 55-60 nsec. Refer to Figure 6 for details on the connection to the

scalars and 850 coincidence analyzer.

Next the two photomultipliers minus the filter and shutter assembly were placed in a highly polished brass block at  $180^\circ$  to each other.

A light source described above was mounted in the opening at the top of the block. The adjustment on the Model 850 Coincidence Analyzer was set for 30 nsec by counting the photons from the light source. The resolving time<sup>54</sup> ( $2t$ ) was calculated by

$$2t = \frac{N}{R_1 R_2} \quad (19)$$

where  $N$  = coincidence rate

$R_1, R_2$  = single rate of each photomultiplier

A tritium source, furnished as a standard by Nuclear Chicago, was placed into the well of the block and counted for a precise time. Next a black bottle, which was simply a bottle filled with black ink, was counted as background. An assumption was made that net coincidence rate of tritium, i.e., coincidence rate of tritium minus the black bottle rate, was due to the tritium. The efficiency was calculated from the following formula:

$$E_T = \frac{\text{cpm}}{\text{dpm}} \quad (20)$$

where cpm = net counts per minute of the tritium source

dpm = disintegration per minute of the tritium source

Changes in the gain, DC level of the output and the high voltage of the power supply were made to optimize  $E_T$ . The final conditions obtained were 2400 VDC on high voltage to resistor network of the photomultipliers, a gain of 10 and DC level of -50 mV which gave  $E_T$  of 25.5%. These settings remained as stated throughout the rest of the experimental work.

The efficiency of 25.5% was low compared to commercial liquid scintillation counters. This was believed mainly due to the distance of 5 cm between the photomultiplier face and the vial. In the commercial systems this distance was about 5 mm or a light pipe was used. Considering the solid angle subtended in above system, an  $E_T$  of 65-70% would have been obtained with equivalent geometry, in good agreement with  $\sim 60\%$   $E_T$  of the Beckman LS-200B.

System 1 as referred to in Figure 2 was used first. A small area of about 5 mm of the 4 mm ID Pyrex tube was viewed, the remaining part of the tube was masked with black tape. The photomultiplier assemblies were mounted  $180^\circ$  to each other. A small light bulb with a blue colored cap was placed as near as possible to the unmasked area. The area containing the tubes, 6 mm tubing, and the light bulb was heavily draped with black cloth to prevent light leakage from the outside. The counting data was obtained from the procedure described in section-Production of Chemiluminescence.

After the initial experiments with System 1, some additional information about the dual emission was desirable. The addition of the TPHC section along with the multichannel analyzer and vacuum system in Figure 3 corresponded to System 2. The advantage of this arrangement was that the life-time of the excited state could be measured directly.<sup>55</sup> The negative outputs of 161 Discriminator was delayed by 1455 delays for both channels. The delays were set equal to the time arrival of the gate pulse from the coincidence analyzer. This was done by taking the positive pulse from the 850 Analyzer with resolving time set at 100 nsec to the external trigger of 545A Scope. The fast negative output of the delays were simultaneously displayed on the 545A Scope. The timing

was set such that the gate was first, followed by the start pulse and then stop pulse. The Instapulser was inserted via a tee and matched cables to the inputs of the 161 Discriminator, thus assuming proper timing pulses. Full scale on TPHC was set to 125 nsec. The output of TPHC was amplified so that if no stop pulse was present, a 10 volt analog signal was sent to the multichannel analyzer. The DB-263 Delay was set to zero, then the stop channel 1455 Delay was adjusted so that output of TPHC was in channel 55-60 of the multichannel analyzer. If channel 60 represented zero time and the resolving time of the coincidence analyzer was set at 100 nsec, then the time scale presented from the TPHC was -50 to 0 to 50 nsec or about 100 channels.

The photomultiplier, light bulb and 2mm ID Pyrex tube arrangement in this setup was the same as described for System 1. A constant current source supplied the voltage to the light bulb for System 1 and System 2. Since the photons from the light bulb were emitted randomly, it was used to determine the resolving time of the 850 Analyzer and to show that TPHC Section was working properly.

## PART III

## RESULTS

1. System 1

The reactions of O-atoms with NO and SO were carried out in the apparatus shown in Figure 2. Since the NO + O reaction should not give dual emission, the NO<sub>2</sub> afterglow was used to check if any unknown variables were not considered. By passing of 10% N<sub>2</sub> - 90% O<sub>2</sub> through the glow discharge, the afterglow was produced by reactions of the type:



The resolving time for coincidence counts is calculated by equation 19 from the counting information obtained by the photons produced from low intensity light bulb. Table II lists the data for the experiments concerned with System 1. The column heading called "Setting" refers to the position of the controls on the coincidence analyzer.

Random and coincidence data were tabulated according to the origin of the emission, such as NO + O, light bulb, or SO + O. When 10% N<sub>2</sub> - 90% O<sub>2</sub> mixture was run, the data are referred to as NO for the NO<sub>2</sub> afterglow. If either COS or CS<sub>2</sub> was added, the SO<sub>2</sub> afterglow was produced and was referred to as SO. Because the data appeared to be identical, no distinction between COS and CS<sub>2</sub> was made. Corning light filters as indicated in the third column of Table II were inserted to isolate parts of the emission spectrum in order to obtain information

TABLE II  
SUMMARY OF COUNTING DATA

Setting	Event	Filter	Press. (mTorr)	Counting Interval (Sec.)	Singles( $\times 10^{-6}$ )		Coincidence	Resolving Time( $10^{-9}$ sec)
					R <sub>1</sub>	R <sub>2</sub>		
0-0	light	0-52	-	10	1.3950	2.6096	4712	12.9
0-0	light	0-52	-	100	2.2709	1.7161	539	13.8
0-0	SO	0-52	40	100	2.9940	2.9126	1639	18.8
0-0	SO	0-52	40	100	2.9906	2.9907	1595	17.8
0-0	SO	0-52	40	100	2.9738	2.8905	1511	17.6
0-10	SO	0-52	40	100	2.9239	2.9005	10865	128.1
0-10	SO	0-52	40	100	2.9367	2.9045	11038	129.4
0-10	SO	0-52	40	100	2.9579	2.9157	11155	129.3
0-10	light	0-52	-	100	1.7494	1.3564	2489	104.9
0-10	light	0-52	-	100	1.8204	1.3858	2669	105.8
1-10	light	0-52	-	60	1.8712	2.4682	67867	881.8
1-10	light	0-52	-	60	2.0973	2.7655	84909	878.4
1-10	SO	0-52	40	120	2.8155	3.3412	71635	913.8
1-10	SO	0-52	40	120	2.7438	3.3464	69800	912.2
0-0	NO	0-52	45	100	8.6340	8.2815	10464	14.6
0-0	NO	0-52	45	100	7.9655	7.4643	8786	14.8
0-0	SO	7-54	40	60	.3922	.4661	61	20.0
0-0	SO	7-54	40	60	.3494	.4051	45	19.1
0-0	light	7-54	-	60	.3358	.7292	82	20.1
0-0	light	7-54	-	60	.3497	.8051	86	18.3
0-0	SO	2-64	40	100	1.9408	1.4421	416	14.9
0-0	SO	2-64	40	100	1.9612	1.4045	396	14.4
0-0	light	2-64	-	100	1.9570	1.4734	407	14.1
0-0	light	2-64	-	100	1.9540	1.4512	418	14.7

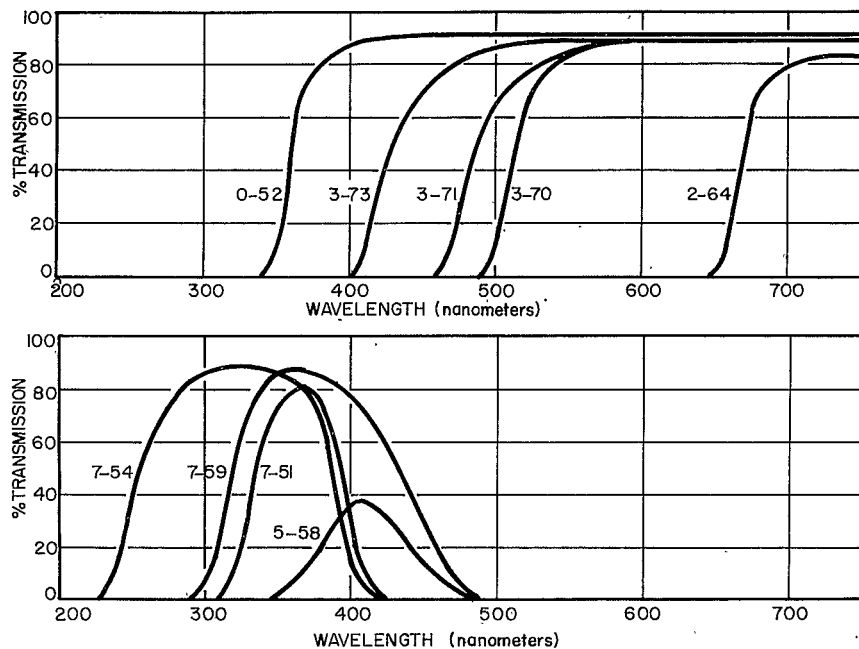


FIGURE 7 CORNING GLASS COLORED FILTERS

about the wavelength region necessary for dual emission. Figure 7 gives the intensity-wavelength curves for the various filters<sup>56</sup> used throughout this work. The resolving time in nanoseconds was calculated from equation 19 for all events and listed under the proper heading.

From Table III, which incorporated a portion of the data in Table II, it can be seen that as the resolving time of the coincidence analyzer is increased, the net coincidence increases, but in addition the per cent increase of net coincidence decreases. The net coincidence is calculated by taking the resolving time of the analyzer, obtaining the accidental rate, and subtracting the coincidence for the SO event from the accidental rate. The decrease in the per cent of net coincidence would indicate that an excited state of a finite lifetime exists. Thus a relationship between the resolving time and net coincidence could give the lifetime of the excited species.

The decay law of emission from an excited state is:

$$I = I_0 e^{-\frac{.693t}{t_{\frac{1}{2}}}} \quad (24)$$

let

$$\tau = \frac{t_{\frac{1}{2}}}{.693}, \text{ lifetime} \quad (25)$$

$N$  = net coincidence

$t_g$  = resolving time ( $t_g - t_0$  where  $t_0 = 0$ )

$t_{\frac{1}{2}}$  = half-life

then

$$N = \int_{t_0}^{t_g} \frac{h\nu}{\text{unit time}} = \int_{t_0}^{t_g} I dt = \int_0^{t_g} I_0 e^{-\frac{t}{\tau}} dt \quad (26)$$

TABLE III  
 THE EFFECT OF INCREASING  
 RESOLVING TIME FOR SO + O COMPARED  
 TO RANDOM EMISSION

Setting	Resolving Time* $t_g$	Net coincidence N	%increase**
0-00	13.4 nsec	4-13 cps	35%
0-10	105.4 nsec	20.17 cps	22%
1-10	880.1 nsec	21.25 cps	21%

\* Resolving time calculated by equation 19 from light bulb data.

\*\* Per cent increase of net coincidence rate over accidental rate.

$$N = -I_0 \tau \left[ e^{-t/\tau} \right]_0^{t_g} \quad (27)$$

$$N = I_0 \tau \left[ 1 - e^{-t_g/\tau} \right] \quad (28)$$

A graphical representation of equation 28 to obtain the lifetime of excited species would be helpful. However, the variables nor the equation allow this to be done conveniently. By assuming  $I_0$  to be constant throughout the measurements, the following relationship is obtained:

$$\frac{N_1}{N_2} = \frac{1 - e^{-t_{g1}/\tau}}{1 - e^{-t_{g2}/\tau}} \quad (29)$$

By substituting in the values  $t_g$  and  $N$  for the three settings given in Table III an average value of lifetime  $\tau$  of the excited state is obtained and was found to be 10 nsec.

By referring to Figure 7 and Table II information about the spectral region for the dual emission was analyzed. Of special significance is the fact that the dual emission was found where it might be expected, while not being observed when not expected due to some inherent instrumentation problem. The observation of all emission was blocked by use of proper filters, then a filter was used where no dual emission form  $SO + O$  could be observed due to energy considerations, and also  $NO + O$  emission was also observed where the same type energy consideration precluded any dual emission to be anticipated. To ascertain that the results were truly due to light emission the 2-64 filters were used where only light in the red beyond the sensitivity of photomultipliers could pass and only thus external noise such as electrical noise from

the discharge or mechanical noise generation in the cables was possible and could not be attributed to the dual emission. The total energy of the two photons emitted from the  $\text{SO} + \text{O}$  recombination reaction cannot have an energy exothermicity of the reaction - 5.61 eV. In System 1 only the 8575 photomultiplier tubes were used, thus the sensitivity extended into the red only to  $6000\text{\AA}$  corresponding to about 2 eV. The 7-54 filter was inserted, where the observed spectral region corresponded to energies greater than 3.5 eV. No dual emission, i.e., an increase in net coincidence or calculated resolving time, was observed. The reaction of  $\text{NO} + \text{O} \rightarrow \text{NO}_2$  is 3.1 eV exothermicity and half would be 1.55 eV ( $7900\text{\AA}$ ) and could not be expected to be observed with these tubes. No net coincidence effect above the accidental rate was found in any of these cases.

## 2. System 2

After some initial experiments with System 1, the decision of adding a time to pulse height converter along with a multichannel analyzer was considered. The value of such additional equipment was that the lifetime of excited species could be calculated directly from the experimental data taken all over the same time interval. The graphical representation of the analog plots obtain in this manner from the stored data in the multichannel analyzer gave substantially the same evidence of the dual emission and lifetime of the excited species. However, the Teflon valve in System 1 started to be attacked by O-atoms, apparently this happened as a result of long exposure to O-atoms. A dead-end tube was designed where the SO radicals and O-atoms could diffuse into the viewing region of the photomultiplier.

FIGURE 8 LIGHT BULB ANALOG PLOT

FIGURE 9 TIME MARKERS

NOT REPRODUCIBLE

FIGURE 10 DUAL EMISSION ANALOG PLOT WITH 0-52 FILTERS

NOT REPRODUCIBLE

FIGURE II DUAL EMISSION ANALOG PLOT 3-73 FILTERS

NOT REPRODUCIBLE

FIGURE 12 DUAL EMISSION ANALOG PLOT WITH 7-51 AND 0-52 FILTERS

NOT REPRODUCIBLE

FIGURE 13 NO DUAL EMISSION ANALOG PLOT 7-59 AND O-52 FILTERS

FIGURE 14 NO DUAL EMISSION ANALOG PLOT WITH 3-71 AND 0-52 FILTERS

NOT REPRODUCIBLE

FIGURE 15 NO DUAL EMISSION ANALOG PLOT WITH 3-70 AND 0-52 FILTERS

NOT REPRODUCIBLE

FIGURE 16 NO DUAL EMISSION ANALOG PLOT WITH 7-51 AND 3-73 FILTERS

TABLE IV  
FIGURE INFORMATION FOR MULTICHANNEL  
ANALYZER PLOTS

Fig.	Event	Filter		Scale Factor	Singles		Coin Rate	MCA Accum. Time
		Start	Stop		$R_1$	$R_2$		
8	Light	0-52	0-52	$10^3$	34802 cps	27599 cps	103 cps	11.46 min
9	TIME MARKERS							
10	SO	0-52	0-52	$10^3$	9044	12716	18.6	40
11	SO	3-73	3-73	$10^2$	4966	5360	3.6	20
12	SO	7-51	0-52	$10^2$	4331	2848	2.3	20
13	SO	7-59	0-52	$10^3$	13327	15299	23.0	20
14	SO	3-71	0-52	$10^3$	7853	9974	8.4	40
15	SO	3-70	0-52	$10^3$	10302	13044	13.5	20
16	SO	7-51	3-73	$10^3$	13921	7840	11.5	20

This provided an alternate arrangement for producing the  $\text{SO}_2$  afterglow than used in the flow system 1. Figures 8-16 represent the data as a linear analog plot from the multichannel analyzer. The x coordinate represents time between emitted photons divided into finite increments as channels and the y coordinate is equal to the number of photons observed in each channel. Table IV is a guide for the various experimental parameters used. Clear evidence of the dual emission process is evident by the peak in the plots. Random light source would give a straight line plot in Figure 8. The centroid of each plot represents zero time and from edge to edge of the plot (the data stored as non-zero data) represents about 100 nsec - the resolving time of the coincidence analyzer. Figure 9 is the placing of time markers generated by equal spacing by the calibrated delay. The spacing of 8 channels per 8 nsec delay gives convenient 1 nsec/channel. From this knowledge, the lifetime of the excited species may be calculated from Figure 10. Since the data for each experiment is also printed out, Figure 17 represents the raw data as a semilog plot, the slope of which gives the lifetime of 8-10 nsec. In the case of Figures 11 and 12, wavelength cutoffs for the light emission from  $\text{SO}_2$  afterglow were conducted. As seen from Figure 7, the 3-73 filters do allow the proper wavelength for dual emission. If a 3-71 filter is inserted as in Figure 14, a photon of greater energy than equivalent wavelength of  $4500\text{\AA}$  is not seen; thus no dual emission is observed. However, Figure 12 cuts off the red photon but retains the blue photon needed. From this information, it may be concluded that the light for dual emission is most likely to be observed in a wavelength interval  $4000\text{\AA} - 4500\text{\AA}$ . Figures 13, 15 and 16 confirm this conclusion.

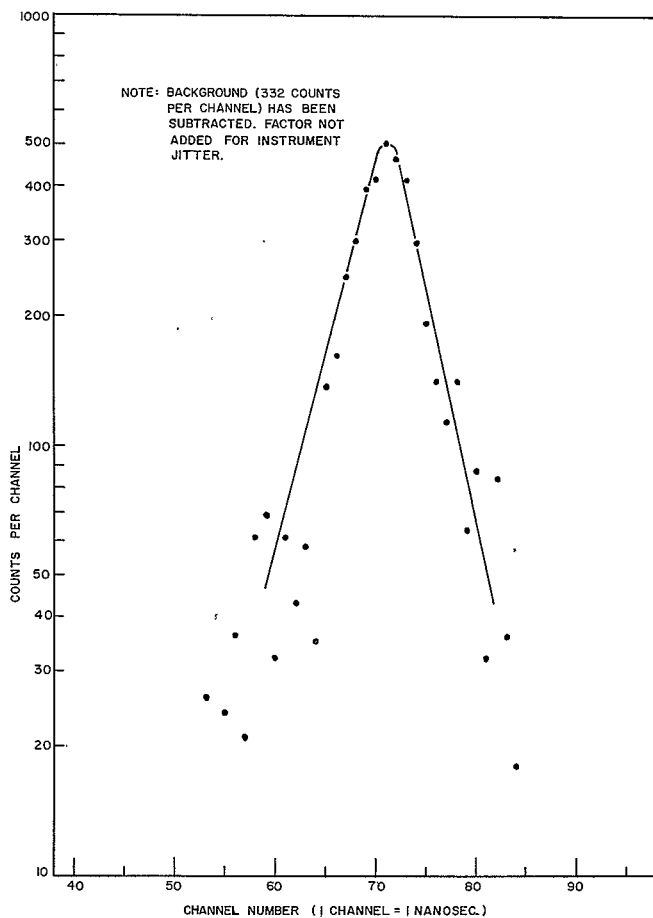


FIGURE 17 HALF-LIFE CURVE FOR DUAL EMISSION OF  $\text{SO} + \text{O}$  CHEMILUMINESCENT REACTION

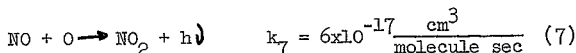
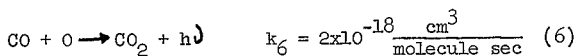
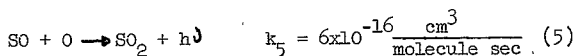
When the  $\text{NO} + \text{O}$  afterglow was run, either by using 10%  $\text{N}_2$  and 90%  $\text{O}_2$  mixtures through the discharge or the addition of pure  $\text{NO}$  into the  $\text{O}$ -atom stream, no dual emission was observed and analog plot was the same in appearance as that given in Figure 8. An attempt to observe the  $\text{CO} + \text{O}$  afterglow was also conducted, but in this case not enough light intensity could be obtained from the  $\text{CO} + \text{O}$  reaction. The count rate increased only by 20% over background. Since no dual emission was observed, no conclusion could be drawn whether or not the process for light emission in reaction 6 was the same reactions 5 and 7. Experimental conditions for reaction 6 probably were not favorable.

The wavelength of  $6000\text{\AA}$  for the RCA 8575 photomultiplier was the limit for observation into the red. A new developmental tube from RCA - C31000F, was installed for several runs. This particular tube had reportedly superior performance out into the infrared region of the spectrum. Observations of  $\text{NO}_2$  and  $\text{SO}_2$  afterglows in both a single counting mode and the coincidence mode as in System 2 give poor performance compared to that expected for this tube. Since the C31000F was a relatively new developmental tube, the single photon counting experiments would have required some time to get optimum performance as was the case of the 8575 tube. The application of this to the experiment was dropped until some quality control studies could be made.

## PART IV

## DISCUSSION OF RESULTS

Various conflicting results on the chemiluminescent recombination reaction of  $\text{NO} + \text{O}$  by various workers have made the mechanism controversial. While the mechanism for the  $\text{SO} + \text{O}$  reaction under light emission is in general agreement. Only three two-body recombination reactions involving light emission have been investigated in detail.



The  $\text{SO} + \text{O}$  reaction (5) was used for the study of dual emission in this thesis for several reasons: the least amount of controversy exists, with regard to the mechanism for the luminescent process, the energy emitted as light is 50% higher than in reaction 7 permitting observation with available instrumentation, and it is a relatively fast reaction and convenient for observation.

If the light emission of reaction 7 in the micron pressure region is measured as a function of the concentration of  $\text{NO}$  and  $\text{O}$ , the results support the two-body recombination mechanism under light emission. The addition of a third-body in the millitorr region will not show any interference for a second order reaction. Advocates for the three-body mechanism involving light emission obviously have to make an additional assumption that the third body depopulates the excited species proportional to concentration of the added third-body. Under this assumption, the order for light emitting process would appear to be second order but

in reality involves a three-body collision. Previous work in this laboratory has shown this assumption to be erroneous; details are discussed elsewhere.<sup>2,6,7</sup> For the investigation of the  $\text{SO} + \text{O}$  reaction, the 100 mTorr pressure range is satisfactory and the experiments can be performed fairly easily. For the  $\text{SO} + \text{O}$  reaction, the  $\text{SO}$  is a product of the reaction between  $\text{O} + \text{COS}$  or  $\text{CS}_2$  where as for the  $\text{NO} + \text{O}$  reaction this is not the case. Even so, the reaction of  $\text{NO} + \text{O}$  is slower and could be measured at a lower pressure. Reliable coincidence data for the  $\text{SO} + \text{O}$  and even  $\text{NO} + \text{O}$  reaction would be difficult to obtain in the 1-20 mTorr region. The necessary sensitivity of the single photon counting is available for this pressure region and the experiments could be performed with relatively less difficulty. However, for the measurement of the lifetime of excited species by coincidence counting a higher pressure region was necessary.

Years ago, the concept of the two-photon emission, as a explanation for some of the misunderstanding in the  $\text{NO} + \text{O}$  recombination reaction mechanism was conceived. Not until recently, however, was adequate electronic equipment developed for pursuing the investigation of dual emission. Recent developments of high speed electronics and high gain photomultipliers have allowed the investigation of dual emission in the  $\text{SO} + \text{O}$  system. The concept of dual emission was discussed in the introduction; it is reinstated here for the two possibilities.

Case I - Two photons are emitted in the time interval of less than  $10^{-9}$  seconds or virtually simultaneously.

Case II - A two-particle recombination product from where a photon is emitted to an excited state. The second quanta is emitted from this state to a state

near one of the low lying vibrational levels in the electronic ground state.

As has been shown, no clear evidence was found for Case I. Evidence indeed for Case II was found, and is probably dominant for the  $\text{SO} + \text{O}$  light emitting recombination process.

The observed emission for  $\text{SO} + \text{O}$  in the first step of Case I is continuous. The second step should have a band structure, but with the continuum superimposed on the overall spectrum. High resolution spectroscopy would be necessary to observe the band structure, however, this would be difficult because of the low intensity per wavelength interval. The same remarks are true for the  $\text{NO} + \text{O}$  reaction. If the second light quanta is emitted, an excited level near the ground state is formed. The emission of the higher energy excited state to lower excited level would almost correspond to one of the microscopic reversibility this reasonable absorption coefficient for the region where the second photon is emitted has to be expected. However, the Franck-Condon principle may substantially reduce the probability for the molecule to come back to the ground state by this emission alone. Indeed, the absorption data of  $\text{SO}_2$ ,<sup>48,57,58</sup> and  $\text{NO}_2$ <sup>48</sup> show this to be true for the  $\text{NO} + \text{O}$  and  $\text{SO} + \text{O}$  systems. If no absorption were measurable, no dual emission would be expected.

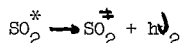
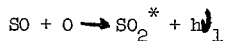
For studying these reactions, photomultipliers with a wide spectra response and a good quantum efficiency are necessary. Even, a good photomultiplier has a quantum efficiency of 1-10% in a limited portion of the spectrum, mainly the visible near U.V. region. The best tubes available today have perhaps 30% quantum efficiency in this region. Geometry, quantum efficiency of the photomultipliers, spectral response

and resolving time must be considered for the efficiency in a coincidence counting system. To give an example of an experimental situation: a reaction vessel emitting  $10^7$  photons/cm<sup>2</sup>.sec., because of efficiency considerations about 10% of the light, would be counted -  $10^6$  counts per second (cps). Therefore, about 1% would be counted as coincidence -  $10^4$  cps. The background rate for coincidence is only a few counts per second, but by counting  $10^5$  cps the accidental counting rate increases substantially as seen in the results section. If the primary photon state has a lifetime in the order of  $10^6$  seconds, the dual emission would be unrecognizable from background. With all the problems considered a high percentage of the light emission must be dual emission.

Indication which prompted this investigation for the two-photon emission included: the light emission of the reaction 5-7 seems basically to be continuous, the low wavelength cut-off as compared to energy in the reaction, and the general shape of the light emission as compared to beta-energy curve. The first thought concerning dual emission process from the information mentioned above was that it might be a simultaneous emission as in Case I. Generally, excited states of molecules have lifetimes of  $10^{-8}$  to  $10^{-6}$  seconds depending upon the energy involved and spin rules. The simultaneous photon emission from molecules is unlikely since the upper limit of the probability is about  $10^{-10}$  for two photons. The normal emission lifetime is in the order of  $10^{-8}$  seconds and the collisional time is  $10^{-13}$  seconds. Thus the probability of simultaneous photon emission would be less than  $10^{-10}$   $\left[ \frac{10^{-13}}{10^{-8}} - \frac{10^{-13}}{10^{-8}} = 10^{-10} \right]$ . Obviously, this is an oversimplification in order to explain the difficulty in trying to observe simultaneous emission. In the experiments conducted for this thesis, the simultaneous

emission was not observed as reported in the results section.

The present results do show that the dual emission happens and can be explained in terms of the following steps:



that is, a primary reaction involving the formation of  $\text{SO}_2$  in an excited state with the loss of part of the energy of recombination due to photon emission followed by emission of the second photon from the excited ( $\text{SO}_2^*$ ), to a lower level ( $\text{SO}_2^\dagger$ ) near the ground state. From the measurements of the lifetime, an average of 10 nsec for excited state  $\text{SO}_2^*$  was obtained. It should be noted that this is not an unique excited state, but a series of states depending on the energy lost by  $h\nu_1$ . Therefore the lifetime of the excited state might be more appropriately termed the lifetime of the excited species. The excited levels of  $\text{SO}_2^*$  are produced with the first photons emitted: the emission of a continuum. As shown in equation 5 the energy of  $\text{SO} + \text{O}$  reaction is 5.61 eV. After the emission of the two light quanta, the  $\text{SO}_2^\dagger$  still may have a few tenths of an electron volt as vibrational energy remaining. The available energy for light emission may not significantly exceed 5 eV. The addition of energy due to the kinetic energy of the recombined particles is the order of  $RT$  or less than 0.1 eV and is practically negligible. Half of the energy available for light emission is 2.5-2.7 eV corresponding to wavelength of 4500-5000 Å. Since the photomultipliers used are sensitive in the red to 6000 Å (2 eV), obviously the two photons must fall between the spectral region of 3600 Å (3.4 eV) and 6000 Å. By the limitation of the total energy in the range

of the counting system, the region where the system is most sensitive for dual counting is between the wavelength  $4500\text{--}5000\text{\AA}$ .

According to Figure 1A, the maximum intensity for photon emission is in the region  $3000\text{\AA}$ . Therefore, care was taken in choosing the light filter system, so that the transparency of the filter would be adequate for the region where the counting system is most sensitive for two photon counting. As shown in the results section, if  $7\text{--}54$  filter is inserted into the counting system (see Figure 7 for transmission curve) the minimum energy would be  $3.0\text{ eV}$ ,  $4000\text{\AA}$ , for the production of the complement second light quanta in the red region where the photomultiplier is not significantly sensitive. Thus the observation of the emission conditions are not compatible with the sensitivity of the equipment used. Then we may conclude that one photon is not blue and the other red, but the primary photon appears shifted to the blue, and the second shifted to the red.

From the results of the  $\text{SO} + \text{O}$  reaction, it is possible to interpret and correlate known experimental facts about the  $\text{NO} + \text{O}$  reaction, if indeed the  $\text{NO} + \text{O}$  recombination under light emission has an analogous mechanism. The reason at least in part for the three-body controversy then appears clear. First, it was apparent that the results of other authors had been due to experimental errors like the neglect of back-diffusion or changing the viscosity of the gas by introducing additives in the  $\text{NO} + \text{O}$  mixture. But now, in addition the dual emission results offer some more gratifying experimental explanation for the interpretation of some of the results. The additive third body may quench individually the excited species,  $\text{NO}_2^*$ , but cannot quench the photon produced simultaneously with the excited state  $\text{NO}_2^*$  because by this

dual emission mechanism the primary photon and excited state are produced simultaneously. The greenish white afterglow at high pressures versus the whitish to gray-white afterglow may be due to the quenching of the  $\text{NO}_2^*$  state. This would be difficult to measure, because the primary photon is persistent. Summing up, many authors may have been misled by the fact that excited species  $\text{NO}_2^*$  was somehow quenched by the additive third-body and were led to assume that introduced substance was necessary for the primary light emission process.

Of the three well known afterglows  $\text{CO}_2$ ,  $\text{NO}_2$  and  $\text{SO}_2$  only  $\text{SO}_2$  was able to produce the dual emission for the measurement techniques employed in this thesis. The  $\text{CO} + \text{O}$  reaction is too slow and would require a large light collection apparatus. Also from the known absorption data of  $\text{CO}_2$  it seems questionable if the dual emission would lie outside the spectrum region of the photomultipliers used. Different techniques would be necessary for the observation of the dual emission in the  $\text{CO} + \text{O}$  reaction: a low pressure is necessary, the reaction could be heated to increase the rate of the reaction, and a large volume for the light emission to be detected. A considerable number of real problems may be anticipated as suggested in the result section.

Obviously, the recombination of  $\text{CO} + \text{O}$  under light emission is one of the most interesting and tempting reactions in the fields of photoluminescence and combustion kinetics. As stated earlier, it was fortunate that  $\text{SO} + \text{O}$  reaction was chosen for the observation of dual photon emission.

With this information and improvement in techniques and ability of photon counting, it seems that in the near future, experiments with the recently developed photomultipliers, such as the C31000F, will

allow the observation of dual emission in the  $\text{NO} + \text{O}$  system, and  
to get further insight of the  $\text{NO} + \text{O}$  light emission mechanism.

## PART V

## CONCLUSIONS

Because of the increasing technological advances in photomultipliers and nuclear instrumentation, the content of this thesis was done at this time. However, several recent advances in the construction and materials of photomultipliers may allow the investigation of two photon processes in other chemical systems. From the experiments conducted, it seems that only the efficiency of light detection systems and the controlling of the chemical reactions were major factors to be considered when observing dual photon emission, if the lifetime of the excited species present is less than 50 nsec.

Up to this time, no double emission reaction process in a molecular species had been observed, the ramification of such a process should add significantly in understanding the mechanism for two-body recombination reactions under light emission. With the use of single crystal GaAs and GaP for photocathodes of photomultiplier tubes, the sensitivity into the infrared region of the spectrum would be about 10 to 50 times better than C31000F tube used in this work. Thus, the  $\text{NO} + \text{O}$  recombination reaction could be investigated for dual emission. All the other conditions that are required for dual emission are satisfied under the same conditions for the  $\text{NO} + \text{O}$  afterglow as for the  $\text{SO} + \text{O}$ . Once the photomultipliers become available, the experiments could be performed to verify the analogies stated here.

## PART VI

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## PART VII

## APPENDIX I

Measurement of the Half-Life of 1.332 MeV State  
 $^{60}_{28}\text{Ni}$  by Delayed Coincidence  
of  $^{60}_{27}\text{Co}$

$^{60}_{27}\text{Co}$  beta decays to the 2.51 MeV level of  $^{60}_{28}\text{Ni}$ . An E2 transition emits a gamma ray of 1.17 MeV to 1.332 MeV level. The Half-life of  $7 \times 10^{-13}$  seconds<sup>59</sup> for this state has been measured from the resonant scattering cross section experiments.<sup>60</sup> However, here an attempt is made to use a delay coincidence technique along with a gamma spectrometer for measurement of the half-life for this short living state. NaI(Tl) crystal were used for scintillation detector followed by standard RCA photomultipliers. The amplifiers, discriminators, and coincidence units were made at Yale back in the middle 1950's. This equipment was the forerunner of the Canberra 800 and 1400 series instruments manufactured at the present time. Referring to Figure 18, the equipment was arranged in a similar manner as described in the experimental section (Part II). The start channel is triggered by 1.17 MeV gamma ray and the stop channel by the 1.332 MeV gamma ray. The detectors are arranged at  $90^\circ$  to each other because of the E2 transition. A photograph of the photomultiplier arrangement is given in Figure 19. The foam as pictured serves two purposes: back scattered gamma rays are reduced because of the lack of a hard surface, and also the detectors are easy to move. Figure 19 actually shows the experimental set up for  $^{133}_{56}\text{Ba}$ , thus the detectors are not mounted at  $90^\circ$ . Time markers were used to calculate the time interval per channel. The results for various runs are sketched in Figure 20. It was quite a surprise to obtain a lifetime for 1.332 MeV

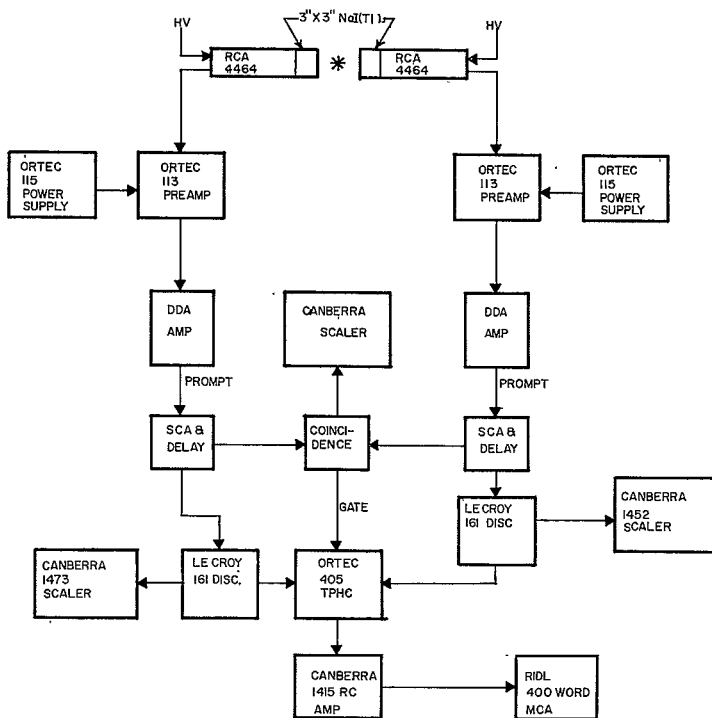


FIGURE 18

FAST GAMMA-GAMMA COINCIDENCE

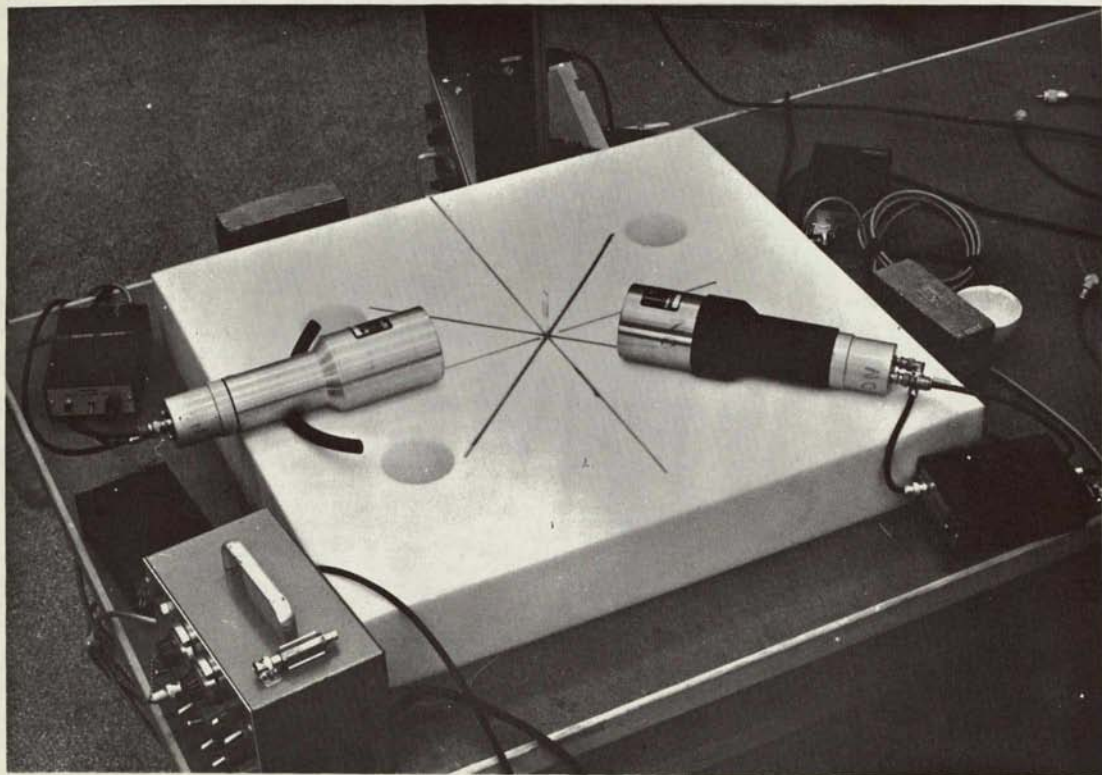


FIGURE 19 PHOTOMULTIPLIER ARRANGEMENT FOR  $^{133}_{56}\text{Ba}$  EXPERIMENT

NOT REPRODUCIBLE

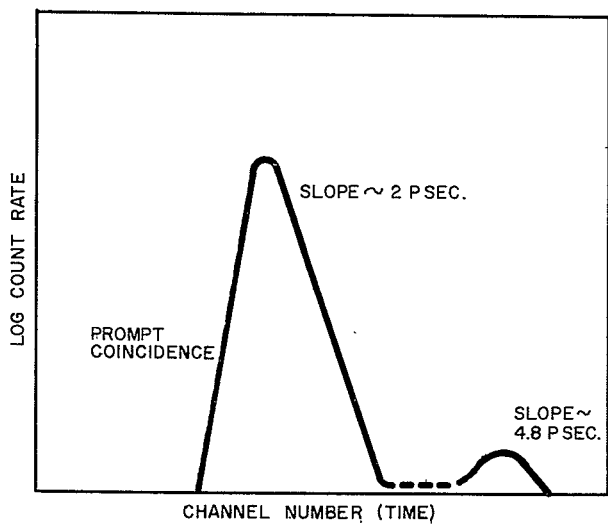


FIGURE 20 TIME RESOLUTION CURVE FOR  
THE 0.7 PSEC. STATE OF  $^{60}_{28}\text{Ni}$

state of 2 psec. The NaI(Tl) detector has a very slow decay, which normally does not allow for fast timing.

One reason for the exceptional results obtained might be the use of high linear amplifiers after the dynode instead of using a time pick-off after the anode signal. Most fast-delay coincidence experiments involve a two-channel system; one for timing, using the anode pulse; the second channel for spectroscopy using the dynode pulse output. However, in this case one channel serves both purposes. Because of the constant linear slope furnished by a high quality amplifier, leading edge timing can be done. The remarkable feature of using this type of setup for fast timing is that the equipment is fairly inexpensive and can be used for a multitude of other experiments. However, intrinsic fast gating and other instrumental conditions can not be excluded when considering the time regime without further detailed study.

## PART VIII

## AFTERWARD

Most likely, a serious attempt will be made by other workers to repeat the results obtained herein. Several difficulties are encountered in performing single photon counting coupled with fast coincidence and have been described in the experimental and discussion of results section. Even when this difficulty is under control, the  $SO + O$  reaction itself is not easy to study at low pressures. The author does not believe that the following may be true for the work described here:

"These are cases where there is not dishonesty involved but where people are tricked into false results by a lack of understanding about what human beings can do to themselves in the way of being led astray by subjective efforts, wishful thinking or threshold interactions. These are examples of pathological science. These are things that attracted a great deal of attention. Usually hundreds of papers have been published upon them. Sometimes they have lasted for fifteen or twenty years and then gradually die away".

- Pathological Science by Langmuir\*

\*Colloquium at the Knolls Research Laboratory, Schenectady, New York  
December 18, 1953.